

Viscosity Index Improvers for Lubricating Oils

POLYVINYL ESTERS OF LONG-CHAIN FATTY ACIDS

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INCREASED industrial and military use of machines operating through wide temperature ranges has developed great interest in lubricating oils having improved viscosity-temperature characteristics. The improvement in the viscosity index which can be obtained from increased refining and from mixing of petroleum stocks is limited, and therefore other methods have been sought. Use of thickening agents in lubricating oils has been especially successful. In particular, addition of certain oil-soluble polymers to a base oil has greatly improved its viscosity index. Among suitable polymers in use today are polybutenes (9, 14), polymethacrylates (8, 15), and polyalkystyrenes (7).

VISCOSITY OF HIGH POLYMER SOLUTIONS

The viscosity of a high-polymer solution (1, 12) depends on the size of the polymer, the extent of the intra- and intermolecular interactions of the polymer molecules, the extent of the interaction between the polymer molecules and the solvent, the concentration of the polymer and the nature of the solvent. In general, because higher molecular volume acts to impede liquid flow, a polymer of a high degree of polymerization gives a solution of higher viscosity than does a low molecular weight polymer. If the intramolecular forces are high and the degree of solvation is low—that is, a “poor” solvent—the internal attracting forces cause the polymer molecules to curl up in compact form; this decreases the effective volume and surface area of contact and gives solutions of low viscosity.

In polymer solutions in which the intra- and intermolecular forces are low and the solvation forces are high—a “good” solvent—each polymer molecule is sheathed by solvent molecules and tends to uncurl into long chains; this increases the effective volume and the surface area of contact and gives solutions of higher viscosity than in a “poor” solvent.

The effect of temperature on the viscosities of solutions of high polymers has been discussed by Alfrey, Bartovics, and Mark (1), who studied polystyrene in various solvent mixtures. They showed that in a “poor” solvent the intrinsic viscosity of flexible chain polymers increases with temperature whereas in a “good” solvent it decreases, and they proposed a mechanism to explain this phenomenon. In a “poor” solvent, an increase in temperature diminishes the strength of the intra- and intermolecular bonding; this increases the surface and volume of the polymer

Polymers and copolymers of vinyl esters of the long-chain fatty acids are of potential commercial interest because the monomers can be easily prepared in good yield from inexpensive and readily available raw materials. As part of a general program of preparation and evaluation, these polymers and copolymers were tested as viscosity index improvers for lubricating oils.

Polyvinyl palmitate, polyvinyl caprylate, and copolymers of vinyl palmitate with vinyl acetate are effective viscosity index improvers for lubricating oils. The improvement caused by the copolymers increases with increased vinyl acetate content. The solubility of the copolymers in lubricating oils decreases as the vinyl acetate content increases; an optimum effect is obtained with a copolymer containing about 25 mole % of vinyl palmitate.

In general, the viscosity index-improving effect of a polymer or copolymer in a lubricating oil is enhanced as the solubility of the polymer decreases and its concentration increases.

molecules, with a resulting increase in intrinsic viscosity. In a “good” solvent also, a temperature rise tends to diminish the intra- and intermolecular bonding, but since the polymer chains are already uncoiled, the reduction in bond strength is necessarily slight. A temperature rise, however, causes a greater weakening of the strong solvent-to-polymer bonds, allowing increased intra- and intermolecular interaction, and, therefore, the net effect is a coiling up of the polymer molecules with a resulting decrease in intrinsic viscosity. Experimentally, these authors used a mixture of a solvent

and a precipitant as the “poor” solvent and the pure solvent as the “good” solvent.

Evans and Young (4) performed experiments similar to those of Alfrey *et al.* (1), but they studied polybutenes in some solvents and in lubricating oils containing varying amounts of castor oil, phthalic acid, and glycol derivatives as the nonsolvents for the polymers, and obtained similar results.

APPLICATION OF THEORY TO VISCOSITY INDEX IMPROVERS

These theories of polymer solutions have a direct bearing on the use of polymers as viscosity index improvers. Three conclusions may be drawn. First, as is experimentally well known, polymers of a high degree of polymerization raise the viscosity index more than does an equal concentration of lower molecular weight polymers. This method of augmenting the effect of a given polymer as a viscosity index improver suffers because high molecular weight polymers may be unstable to shearing forces during use, thus limiting the degree of polymerization of polymers that can be utilized. Second, a polymer for which an oil is a “poor” solvent will be a better viscosity index improver than one for which the oil is a “good” solvent. Further, the greater the concentration of polymer in a “poor” solvent, the greater will be the viscosity index improvement. Third, as was also concluded by Evans and Young (4), any method by which the solubility of a polymer in a lubricating oil may be decreased will increase the viscosity index-improving effect of the polymer.

The solvent powers of the lubricating oils must necessarily be considered as essentially constant, because addition of large amounts of nonsolvents, such as those used by Evans and Young (4), would greatly increase the cost of the oil. However, if two monomers are available, and the homopolymer of one is highly soluble and that of the other is insoluble in petroleum oils, then

the copolymers should be expected to have a graded solubility. In effect, this is the converse of the system used by Alfrey *et al.* (1) and by Evans and Young (4).

In the present investigation, the composition of the solvent (the lubricating oil) was kept constant while the insolubilizing fraction of the copolymers was increased, whereas in the works cited (1, 4), the composition of the polymer was kept constant and the insolubilizing fraction of the solvent was increased. It is obvious that there will be an optimum copolymer composition, determined on the one hand by the desirability of decreased solubility and, on the other hand, by the desirability of increased concentration.

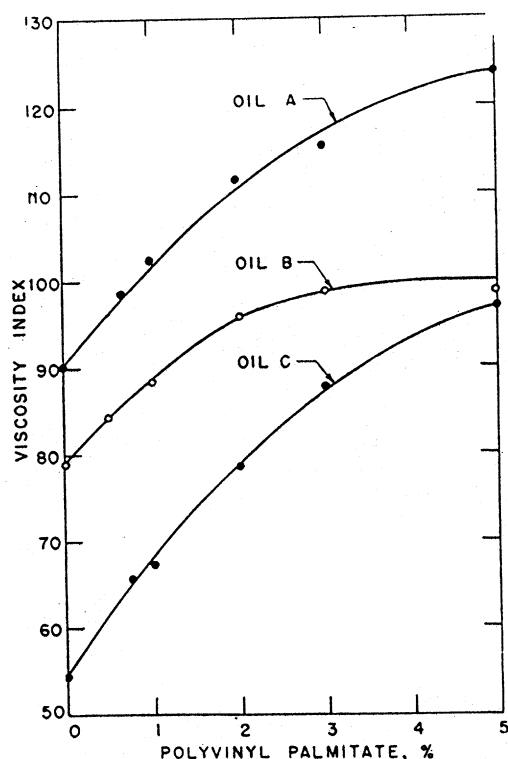


Figure 1. Viscosity Index of Lubricating Oils Containing Polyvinyl Palmitate

This paper describes the use of relatively new polymers, the polyvinyl esters of the long chain fatty acids, as viscosity index improvers. [Wulff and Breuers (16) and I. G. Farbenindustrie (5) mentioned the use of some polyvinyl esters in lubricating oils but gave few data.] Because the vinyl esters are easily made in good yield (11, 13) from inexpensive and readily available raw materials (acetylene or vinyl acetate and fatty acids), they are potentially low cost monomers. Furthermore, these monomers can be polymerized (10) and copolymerized readily to give products of wide applicability. Therefore, studies of the uses of these polymers and copolymers may be of industrial importance.

The polymers used in this study were polyvinyl caprylate and polyvinyl palmitate. These were selected as representative of a liquid and a solid polymer and of a moderately long and a long-chain fatty acid.

The copolymer system chosen for study was vinyl acetate and vinyl palmitate. Polyvinyl acetate is insoluble in petroleum solvents and represents the insolubilizing portion of the copolymer. Vinyl palmitate was chosen as the comonomer because the resulting average chain length of the acyl radicals in the copolymer was approximately that in polyvinyl caprylate, which gave good results. In addition to the possibility of imparting significant increases to the viscosity index, the copolymers also have

the potential advantage of a lower molecular weight for the same degree of polymerization and lower costs than do the homopolymers.

PREPARATION OF POLYMERS AND COPOLYMERS

The polymeric materials used in this study were prepared in solution to control the degree of polymerization. For a degree of polymerization of about 400, a solution of 1 mole of monomer and 0.5 mole % of benzoyl peroxide as the initiator in 2.5 moles of benzene was heated for about 7 hours at 75° C. in a stream of nitrogen. Conversion to polymer was 60 to 70%. The palmitate was freed of monomer by two precipitations with acetone from benzene solutions; methanol was employed as the precipitant for the caprylate. Because the palmitate precipitated as a solid and did not occlude solvent, it was readily freed of adhering solvent by air and vacuum drying. The caprylate was freed of solvent by allowing its benzene solution to evaporate to dryness first at room temperature and then in a vacuum oven at 100° C. As determined by the light-scattering technique, the caprylate had a weight average molecular weight of 73,000, and the palmitate, 119,000.

To obtain a polymer having a degree of polymerization of about 100, ethylbenzene—a more efficient chain transfer agent—was used. Polyvinyl caprylate having a molecular weight of 20,000 was prepared by heating the monomer with an equimolar amount of ethylbenzene and 0.5 mole % of benzoyl peroxide for 12 hours at 75° C. The purification and isolation techniques were the same as for the higher molecular weight polymer. The yield of polymer was 60%.

Copolymers of vinyl palmitate and vinyl acetate were prepared in 3:1, 1:1, and 1:3 molar proportions by heating the appropriate monomer mixtures and 0.5 mole % of benzoyl peroxide in 2.5 moles of benzene for 7 hours at 70° to 73° C. The copolymers were freed of monomers by three precipitations with methanol from benzene solution. Solvent was removed by the frozen-benzene technique (6). The yields of the copolymers were about 60%. The weight average molecular weights of the copolymers containing 75 and 50 mole % of vinyl palmitate were 95,000 and 92,000, respectively.

PREPARATION OF TEST SOLUTIONS

Table I shows the viscosity and pour point properties of the untreated oils used. The viscosity indexes were calculated from the tables of Dean and Davis (8).

TABLE I. EFFECT OF POLYVINYL ESTERS ON VISCOSITY AND POUR POINT

Polyvinyl Ester (5% Solution)	Approx. Degree of Polymer- ization	Viscosity, Cs.		Viscosity Index (3)	Pour Point (2)
		100° F.	210° F.		
		Oil A ^a			
None	...	33.13	5.17	90.2	25
Caprylate	400	57.61	9.01	131.9	25
Caprylate	100	45.24	5.81	112.4	..
Palmitate	400	59.15	8.65	123.7	40
Palmitate-acetate (75/25)	400	49.25	7.97	130.6	40
Palmitate-acetate (50/50)	500	54.08	8.61	132.5	..
Palmitate-acetate (25/75)	...	36.07	6.47	136.5	..
Oil B ^b					
None	...	110.8	10.38	79.1	0
Caprylate	400	139.7	14.98	113.1	5
Caprylate	100	135.9	12.26	86.0	..
Palmitate	400	182.9	16.12	98.5	45
Palmitate-acetate (75/25)	400	141.1	14.32	106.6	45
Palmitate-acetate (50/50)	500	140.3	14.05	104.7	..
Oil C ^c					
None	...	71.50	7.24	54.5	25
Caprylate	400	137.2	13.31	98.9	25
Caprylate	100	96.18	9.47	78.9	..
Palmitate	400	125.7	12.34	96.7	40
Palmitate-acetate (75/25)	400	122.6	12.12	96.0	35
Palmitate-acetate (50/50)	500	122.1	12.07	95.8	..

^a Pennsylvania 150 neutral.

^b Solvent-refined mid-continent neutral.

^c Acid-refined mid-continent neutral.

The polyvinyl caprylate and the polyvinyl palmitate having degrees of polymerization of about 400 were used to make solutions containing 0.5, 1, 2, 3, and 5% of polymer in each of the three test oils. Because the rate of viscosity index improvement with respect to concentration appeared to diminish at about 5% (Figures 1 and 2), only solutions containing 5% of polymer were made from the lower molecular weight polyvinyl caprylate and from the copolymers. The solubility of the 25:75 copolymer (palmitate:acetate) was less than 3% in oils B and C, and therefore the copolymer was not tested in these oils. The 5% polyvinyl palmitate and the 5% 25:75 copolymer solution became heterogeneous on long standing at room temperature.

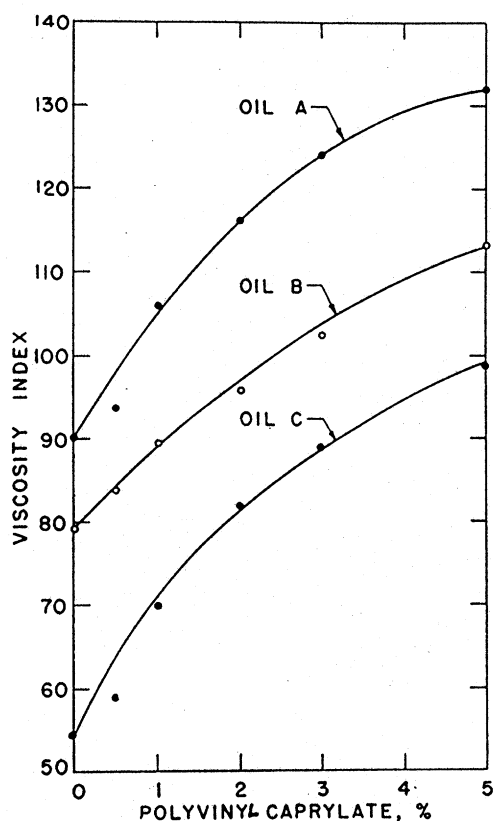


Figure 2. Viscosity Index of Lubricating Oils Containing Polyvinyl Caprylate

RESULTS AND DISCUSSION

Figures 1 and 2 show the effect of increasing concentrations of the two polymers having a degree of polymerization of about 400 on the viscosity index of the three base oils. It may be seen that increasing the concentration of the polymers increases the viscosity index and that the rate of improvement declines at about 5%.

Table I gives the viscosity, viscosity index, and pour point data for the solutions containing 5% of all the polymers tested. These data demonstrate that both polyvinyl caprylate and polyvinyl palmitate having a degree of polymerization of about 400 are effective as viscosity index improvers. When used in 5% concentration, each polymer improved the viscosity properties of the base oils sufficiently to increase the S.A.E. rating from 10 to 20-20 W, from 30 to 40, and from no rating to S.A.E. 30. Of the two polymers, polyvinyl caprylate showed the better properties, because it had a greater effect on the viscosity index and did not raise the pour point. Polyvinyl caprylate having a degree of polymerization of about 100 did not exhibit any appreciable viscosity index improving qualities when used in 5% concentration.

TABLE II. EFFECT OF HEATING AT 300° F. FOR 100 HOURS

Polyvinyl Ester, 5% Concn.	Viscosity, Cs.				Viscosity Index	
	Initial		Final ^a		Initial	Final ^a
	100° F.	210° F.	100° F.	210° F.		
Control (base oil B)	110.8	10.38	118.3	10.73	79.1	77.2
Caprylate	139.7	14.98	147.7	13.29	113.1	90.9
Palmitate-acetate (75/25)	141.1	14.32	158.7	13.44	106.6	84.5

^a After heating at 300° F. for 100 hours.

The changes in viscosity index and in viscosity at 100° F. in oil A produced by the copolymers as compared with the changes produced by polyvinyl palmitate are in accord with the theory of viscosity index improvement by polymers. The viscosity index increases and the viscosity at 100° F. decreases as the acetyl content of the copolymer is increased. In oil B, too, the viscosity index improvement caused by the copolymers is greater than that caused by polyvinyl palmitate, but the viscosity index improvement is not correlated with acetyl content. In oil C, the copolymers did not cause any greater increase in the viscosity index than did polyvinyl palmitate, but did cause a decrease in the viscosity at 100° F.

Table II shows the effect of heating one of the test oils and solutions of one of the copolymers and one of the homopolymers in the same oil for 100 hours at 300° F. in air. This test is intended to simulate the useful life of a lubricating oil. At the end of the heating period, the viscosity index decreased in all cases but the viscosity index of the oils containing additive still was significantly higher than that of the untreated oil.

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LITERATURE CITED

- (1) Alfrey, T., Bartovics, A., and Mark, H., *J. Am. Chem. Soc.*, **64**, 1557 (1942).
- (2) Am. Soc. for Testing Materials, Philadelphia ASTM Standards 1949, Part 5, pp. 736-9 (1949).
- (3) Dean, E. W., and Davis, G. H. B., *Chem. & Met. Eng.*, **36**, No. 10, 618 (1929).
- (4) Evans, H. C., and Young, D. W., *IND. ENG. CHEM.*, **39**, 1676 (1947).
- (5) I. G. Farbenindustrie, A.-G., Ger. Patent 600,722 (Feb. 15, 1936).
- (6) Lewis, F. M., and Mayo, F. R., *IND. ENG. CHEM., ANAL. ED.*, **17**, 134 (1945).
- (7) Mikeska, L. A., and Fulton, S. C., U. S. Patent 2,072,120 (March 2, 1937).
- (8) Neher, H. T., and Hollander, C. S., *Ibid.*, **2**, 114,233 (1938).
- (9) Otto, M., and Mueller-Cunardi, M., *Ibid.*, **2**, 130,507 (Sept. 20, 1938).
- (10) Port, W. S., Hansen, J. E., Jordan, E. F., Dietz, T. J., and Swern, D., *J. Polymer Sci.*, **6**, in press.
- (11) Reppe, W., Ger. Patent 588,352 (Nov. 15, 1933).
- (12) Schmidt, A. X., and Marlies, C. A., "Principles of High Polymer Theory and Practice," pp. 77-82, 247-50, New York, McGraw-Hill Book Co., 1948.
- (13) Swern, D., and Jordan, E. F., *J. Am. Chem. Soc.*, **70**, 2334 (1948).
- (14) Thomas, R. M., Zimmer, J. C., Turner, L. B., Rosen, R., and Frohlich, P. K., *IND. ENG. CHEM.*, **32**, 299 (1940).
- (15) Van Horne, W. L., *Ibid.*, **41**, 952 (1949).
- (16) Wulff, C., and Breuers, M., U. S. Patent 2,020,714 (Nov. 12, 1935).

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